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Ruthenium Porphyrins Containing Nitrosyl, Nitrosamine, Thiolate, and Amine Ligands

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It is well-known that NO binds to the heme groups of Hb, Mb, and guanylyl cyclase to form (porphyrin)Fe(NO) species.[1−3] Appel and co-workers have also shown that nitrosamines (R_2NNO) bind to ferric liver microsomal cytochrome P450 to give spectra indicative of (i) binding of the nitrosamine to the substrate pocket (type I) and/or (ii) binding of the nitrosamine directly to the sixth coordination site of the heme moiety (type II).[4] Furthermore, they showed that reduction of these ferric nitrosamine complexes generates iron nitrosyl porphyrin derivatives.[4] Six-coordinate (porphyrin)Fe(NO)(SR) thiolate complexes may also form when NO binds to cytochrome P450[5] or NO synthase.[6] We recently reported the synthesis of a bis(nitrosamine) complex of an iron porphyrin in which the nitrosamine ligands are bound to the paramagnetic Fe(III) center via their oxygen atoms.[7] We were interested in the extension of this chemistry to encompass the preparation of nitrosyl and nitrosamine derivatives of ruthenium porphyrins. We now show that the readily preparable and air-stable $[(OEP)Ru(NO)(H_2O)]^+$ cation is a suitable and convenient precursor to novel diamagnetic nitrosyl porphyrins containing nitrosamine, thiolate, and amine ligands.[8−10]

Reaction of (OEP)Ru(CO) (**1**) with $NO^+BF_4^-$ in CH_2Cl_2 generates $[(OEP)Ru(NO)]^+$, which is recrystallized in air to give the aqua complex $[(OEP)Ru(NO)(H_2O)]^+$ (**2**) in 71% yield (Scheme 1).[11] The ν_{NO} of the complex is at 1853 cm^{-1} (KBr), and the linearity of the Ru−NO linkage (171.0(7)°) has been determined by single-crystal X-ray crystallography.[12] Reaction of **2** with diethylnitrosamine produces the air-stable $[(OEP)Ru(NO)(Et_2NNO)]^+$ (**3**) cationic complex in 82% yield.[13] The ν_{NO} of the complex at 1847 cm^{-1} (KBr) is slightly lower than that for the aqua complex and is consistent with a linear Ru−NO linkage. IR bands of **3** at 1250 and 1201 cm^{-1} shift to 1233 and 1194 cm^{-1}, respectively, upon substitution with $Et_2N^{15}NO$. Upon substitution with $Et_2NN^{18}O$, only the band at 1250 cm^{-1} shifts (to 1240 cm^{-1}). We thus assign the 1250 and 1201 cm^{-1} bands as $\nu_{N=O}$ and ν_{N-N}, respectively, of the coordinated nitrosamine.[14−16] Although we could not obtain suitable crystals of **3** for X-ray diffraction studies, we were able to prepare and isolate the isoelectronic carbonyl analog $(OEP)Ru(CO)(Et_2NNO)$ (**4**) in 71% yield by reaction of **1** with diethylnitrosamine.[17] The IR spectrum of **4** reveals the ν_{CO} at 1909 cm^{-1}, and bands at 1300 and 1256 cm^{-1} that are similarly assigned as $\nu_{N=O}$ and ν_{N-N}, repectively, of the coordinated nitrosamine (the use of $Et_2N^{15}NO$ shifts these bands to 1286 and 1247 cm^{-1}, whereas the use of $Et_2NN^{18}O$ shifts the 1300 cm^{-1} band to 1287 cm^{-1} (sh)). The molecular structure of **4** (Scheme 1) shows that the nitrosamine ligand is bound through its oxygen atom to the formally Ru(II) center in an η^1-O fashion, and the nitrosamine N═O and N−N bond lengths of 1.245(11) and 1.286(11) Å in **4** suggest a contribution of the dipolar $^-O-N=N^+R_2$ structure similar to that suggested previously for the bound nitrosamines in $[(TPP)Fe(Et_2NNO)_2]^+ClO_4^-$.[7] The carbonyl ligand in **4** is readily displaced by 1 equiv of $NO^+BF_4^-$ in $CDCl_3$ to give **3** in quantitative yield by ^1H NMR and IR spectroscopy. The nitrosamine ligand in **3** may then be displaced by diethylamine in CH_2Cl_2 to form the nitrosyl amine

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(1) (a) Moncada, S.; Palmer, R. M. J.; Higgs, E. A. *Pharmacol. Rev.* **1991**, *43*, 109. (b) Clarke, M. J.; Gaul, J. B. *Struct. Bonding* **1993**, *81*, 147. (c) Butler, A. R.; Williams, D. L. H. *Chem. Soc. Rev.* **1993**, *22* (4), 233.

(2) Richter-Addo, G. B., Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992; Chapter 6.

(3) Yu, A. E.; Hu, S.; Spiro, T. G.; Burstyn, J. N. *J. Am. Chem. Soc.* **1994**, *116*, 4117.

(4) Appel, K. E.; Ruf, H. H.; Mahr, B.; Schwarz, M.; Rickart, R.; Kunz, W. *Chem.-Biol. Interact.* **1979**, *28*, 17.

(5) (a) Hu, S.; Kincaid, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 2843. (b) Shiro, Y.; Fujii, M.; Iizuka, T.; Adachi, S.-I.; Tsukamoto, K.; Nakahara, K.; Shoun, H. *J. Biol. Chem.* **1995**, *270*, 1617. (c) Delaforge, M.; Servent, D.; Wirsta, P.; Ducrocq, C.; Mansuy, D.; Lenfant, M. *Chem.-Biol. Interact.* **1993**, *86*, 103. (d) Khatsenko, O. G.; Gross, S. S.; Rifkind, A. B.; Vane, J. R. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 11147.

(6) (a) Hurshman, A. R.; Marletta, M. A. *Biochemistry* **1995**, *34*, 5627. (b) Wang, J.; Rousseau, D. L.; Abu-Soud, H. M.; Stuehr, D. J. *Proc. Natl. Acad. Sci. U.S.A.* **1994**, *91*, 10512.

(7) Yi, G.-B.; Khan, M. A.; Richter-Addo, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 7850.

(8) Satisfactory analytical data (±0.4% for C, H, N, Cl) were obtained for the new complexes **2**−**7**. Full synthesis and characterization details (NMR, IR, and mass spectral data; elemental analyses) are deposited as Supporting Information. OEP = octaethylporphyrinato dianion.

(9) Other ruthenium nitrosyl porphyrins reported: (a) Srivastava, T. S.; Hoffman, L.; Tsutsui, M. *J. Am. Chem. Soc.* **1972**, *94*, 1385. (b) Massoudipour, M.; Pandey, K. K. *Inorg. Chim. Acta* **1989**, *160*, 115. (c) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015.

(10) The electrochemistry of $[(TPP)Ru(NO)(H_2O)]^+$ (TPP = *meso*-tetraphenylporphyrinato dianion) has been described: Kadish, K. M.; Adamian, V. A.; Van Caemelbecke, E.; Tan, Z.; Tagliatesta, P.; Bianco, P.; Boschi, T.; Yi, G.-B.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1996**, *35*, 1343.

(11) Data for **2**: ^1H NMR ($CDCl_3$) δ 10.52 (s, 4H, *meso*-H), 4.22 (q, J_{HH} = 7 Hz, 16H, CH_2CH_3 of OEP), 2.01 (t, J_{HH} = 7 Hz, 24H, CH_2CH_3 of OEP), peak for H_2O not observed; low-resolution mass spectrum (FAB) *m/z* 682 $[(OEP)Ru(NO)(H_2O)]^+$ (9%), 664 $[(OEP)Ru(NO)]^+$ (100%).

(12) The related $[(TPP)Fe(NO)(H_2O)]^+ClO_4^-$ and $[(OEP)Fe(NO)]^+ClO_4^-$ complexes have linear Fe−N−O linkages: Scheidt, W. R.; Lee, Y. J.; Hatano, K. *J. Am. Chem. Soc.* **1984**, *106*, 3191.

(13) Data for **3**: ^1H NMR ($CDCl_3$) δ 10.46 (s, 4H, *meso*-H), 4.20 (q, J_{HH} = 7 Hz, 16H, CH_2CH_3 of OEP), 1.97 (t, J_{HH} = 7 Hz, 24H, CH_2CH_3 of OEP), 1.94 (q, J_{HH} = 7 Hz, 2H, CH_2CH_3 (overlap with OEP)), 0.58 (q, J_{HH} = 7 Hz, 2H, CH_2CH_3), −0.50 (t, J_{HH} = 7 Hz, 3H, CH_2CH_3), −1.98 (t, J_{HH} = 7 Hz, 3H, CH_2CH_3); low-resolution mass spectrum (FAB) *m/z* 766 $[(OEP)Ru(NO)(Et_2NNO)]^+$ (2%), 664 $[(OEP)Ru(NO)]^+$ (100%).

(14) Free nitrosamines display ν_{NO} and ν_{NN} in the 1460−1425 and 1150−1030 cm^{-1} regions, respectively: Williams, R. L.; Pace, R. J.; Jeacocke, G. J. *Spectrochim. Acta* **1964**, *20*, 225.

(15) We have prepared a compound tentatively formulated as $[(TPP)Fe(NO)(Et_2NNO)]^+ClO_4^-$ from the reaction of $[(TPP)Fe(Et_2NNO)_2]^+ClO_4^-$ with NO gas. The IR spectrum of the complex shows a unique Fe−NO stretch at 1919 cm^{-1} and nitrosamine ν_{NO} and ν_{NN} bands at 1267 and 1252 cm^{-1}, respectively. However, this compound is prone to NO loss: Chen, L.; Yi, G.-B. Unpublished observations.

(16) $Et_2N^{15}NO$ was obtained from Isotec Inc. $Et_2NN^{18}O$ was prepared in a manner similar to that used for the preparation of $Me_2NN^{18}O$: Keefer, L. K.; Hrabie, J. A.; Hilton, B. D.; Wilbur, D. *J. Am. Chem. Soc.* **1988**, *110*, 7459.

(17) Data for **4**: ^1H NMR ($CDCl_3$) δ 9.96 (s, 4H, *meso*-H), 4.20 (q, J_{HH} = 7 Hz, 16H, CH_2CH_3 of OEP), 3.40 (q, J_{HH} = 7 Hz, 2H, CH_2CH_3), 2.64 (q, J_{HH} = 7 Hz, 2H, CH_2CH_3), 1.89 (t, J_{HH} = 7 Hz, 24H, CH_2CH_3 of OEP), 0.91 (t, J_{HH} = 7 Hz, 3H, CH_2CH_3), 0.24 (t, J_{HH} = 7 Hz, 3H, CH_2CH_3); low-resolution mass spectrum (FAB) *m/z* 662 $[(OEP)Ru(CO)]^+$ (88%), 634 $[(OEP)Ru]^+$ (100%).

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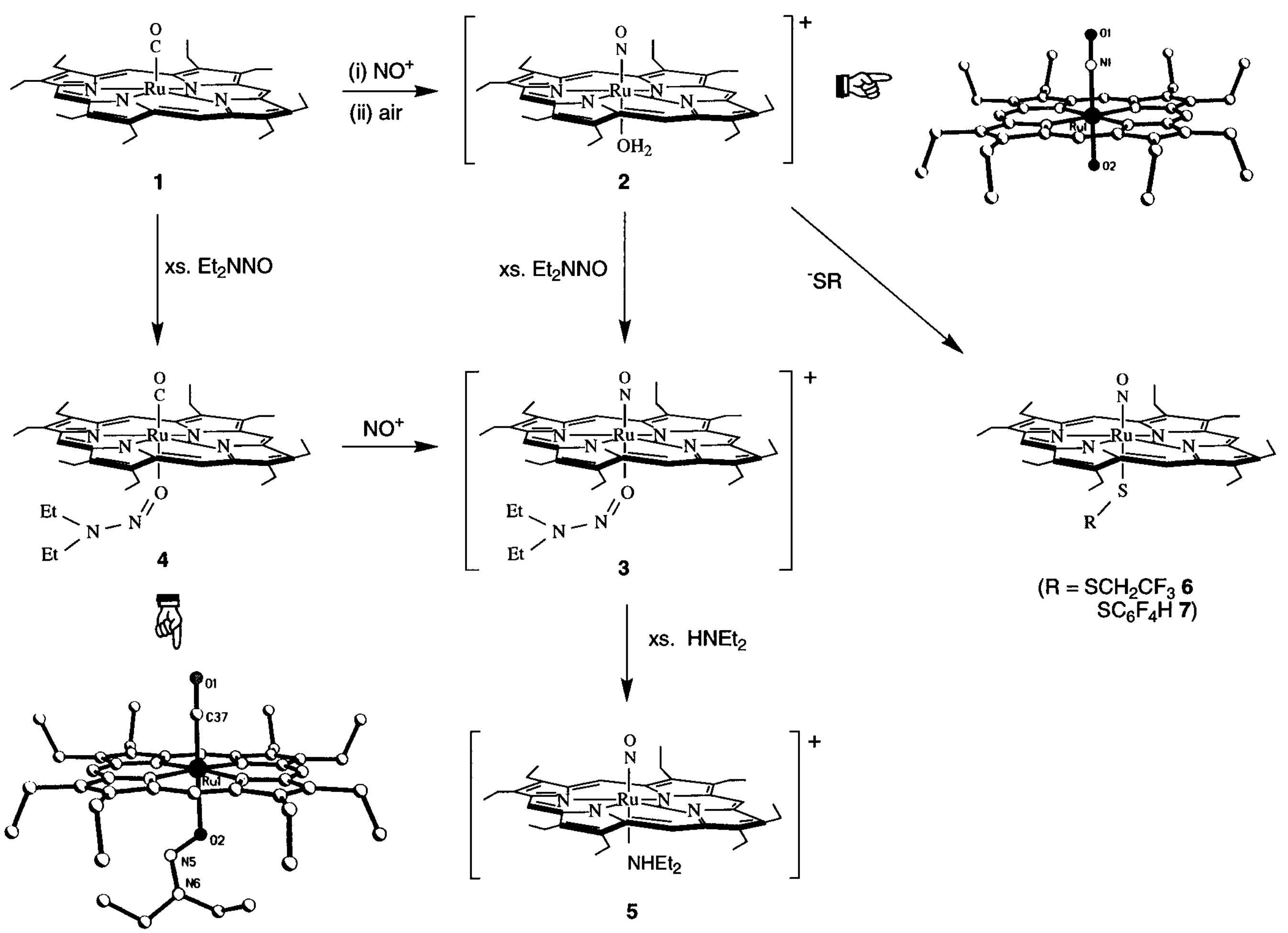
Scheme 1



complex $[(OEP)Ru(NO)(Et_2NH)]^+$ (**5**) in 71% yield.[18] Complex **5** is also obtained directly from the reaction of **2** with diethylamine in 78% yield.

Although complexes of the form (porphyrin)metal(NO)(SR) are potential models for the interaction of NO with cytochrome P450 and NO synthase, no such isolable complexes had been reported prior to this study. We obtained thermally stable nitrosyl thiolate complexes by the reaction of **2** with both alkane- and arenethiolate anions in THF to produce (OEP)Ru(NO)(SR) ($R = CH_2CF_3$ (**6**), C_6F_4H (**7**)) in 81% and 73% yields, respectively.[19,20] These nitrosyl thiolate complexes are moderately air-stable, showing no signs of decomposition in air in the solid state even after 1 week. The IR spectra indicate that the υ_{NO}'s of **6** and **7** are at 1782 and 1798 cm^{-1}, respectively.

In concluding, we note that **3** and **4** are the first mononitrosamine metalloporphyrin complexes to be reported and are also the first metal−nitrosamine complexes containing π-acid ligands (CO, NO^+) to be prepared. Reactions designed for the activation of the bound nitrosamines and extensions of this work to the related iron analogs are in progress.

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Supporting Information Available: Text giving characterization data for complexes **2**−**7** and listings of experimental details for the crystal structure determinations and refinements, thermal ellipsoid drawings, and tables of atomic coordinates, anisotropic thermal parameters, hydrogen coordinates, bond distances and angles, and selected torsion angles and least squares planes for $\mathbf{2}BF_4\cdot H_2O$ and **4** (38 pages). Ordering information is given on any current masthead page.

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(18) Data for **5**: ^1H NMR ($CDCl_3$) δ 10.37 (s, 4H, *meso*-H), 4.17 (m, 16H, CH_2CH_3 (OEP)), 1.99 (t, $J_{HH} = 7$ Hz, 24H, CH_2CH_3 (OEP)), 0.95 (br, 4H, $HN(CH_2CH_3)_2$), −0.57 (br, 6H, $HN(CH_2CH_3)_2$), signal of $HN(CH_2CH_3)_2$ not observed; low-resolution mass spectrum (FAB) *m/z* 736 $[(OEP)Ru(NO)(HN(CH_2CH_3)_2)]^+$ (trace), 664 $[(OEP)Ru(NO)]^+$ (100%).

(19) Data for **6**: ^1H NMR ($CDCl_3$) δ 10.29 (s, 4H, *meso*-H), 4.15 (q, $J_{HH} = 7$ Hz, 16H, CH_2CH_3 of OEP), 1.97 (t, $J_{HH} = 7$ Hz, 24H, CH_2CH_3 of OEP), −2.87 (q, $J_{HF} = 11$ Hz, 2H (SCH_2CF_3)); low-resolution mass spectrum (FAB) *m/z* 779 $[(OEP)Ru(NO)(SCH_2CF_3)]^+$ (2%), 664 $[(OEP)Ru(NO)]^+$ (100%).

(20) Data for **7**: ^1H NMR ($CDCl_3$) δ 10.25 (s, 4H, *meso*-H), 6.00 (m, 1H, *p*-H, SC_6HF_4), 4.13 (q, $J_{HH} = 7$ Hz, 16H, CH_2CH_3 of OEP), 2.00 (t, $J_{HH} = 7$ Hz, 24H, CH_2CH_3 of OEP); low-resolution mass spectrum (FAB) *m/z* 845 $[(OEP)Ru(NO)(SC_6HF_4)]^+$ (3%), 664 $[(OEP)Ru(NO)]^+$ (100%).